International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.9, pp 514-524, 2017

Kinetics of Ir(III)-Catalysed Oxidation of Ampicillin by $Cu(Bip)_2^{2+}$ in Alkaline Medium: A Spectrophotometric Study

Ashok Kumar Singh*, RupamYadav, Jaya Srivastava, Ritu Swamini Bala, Ranju Pradhan, Shahla Rahmani

Department of Chemistry, University of Allahabad, Allahabad- 211002, India

Abstract : Kinetics and mechanism of Ir(III)-catalyzed oxidation of ampicillin by $Cu(Bip)_2^{2+}$ in alkaline medium was studied at 35 ± 0.1^0C. First-order kinetics with respect to [Cu(II)], [Ir(III)] and [OH^-] throughout their variation were observed. The reaction shows fractional positive order kinetics in [Ampicillin]. Nil effect of [bipyridyl] on the rate of oxidation by $Cu(Bip)_2^{2+}$ was observed. The reaction also shows slight increase in the rate by decreasing dielectric constant of the medium and remains unaffected by the change in ionic strength of the medium. The reaction was studied at four different temperatures and observed values of rate constants were utilized to calculate various activation parameters specially the entropy of activation ($\Delta S^{\#}$). $Cu(Bip)_2^{2+}$, ampicillin as such and $[IrCl_3(H_2O)_2OH]^-$ have been assumed as the reactive species of Cu(II), ampicillin and Ir(III) chloride in alkaline medium, respectively. With the help of the observed kinetic orders with respect to the reactants involved in the reaction, spectrophotometric evidence collected for the formation of reactive complexes and the positive entropy of activation, a most probable reaction mechanism for the oxidation of ampicillin by $Cu(Bip)_2^{2+}$ in alkaline medium using Ir(III) as homogeneous catalyst has been proposed.

Key words : Ampicillin, copper-bipyridyl complex, catalysis, spectrophotometric study, alkaline medium.

Introduction

In recent years, kinetic investigations of the oxidation of antibiotics have been performed by using various oxidants because of their medicinal significance. The oxidation of antibiotics by Cu(II)[1], diperiodatoargentate (III)[2], chlorimine-T[3] and hexacyanoferrate(III)[4]have been reported in alkaline media. Literature showsthat copper complexes play important roles in various fields such as catalysis[5],oxidation chemistry[6] and biochemistry[7]. In a recent study, it is reported that copper(II) complexes of N-(methylpyridin-2-yl)-amidino-O-methylurea[8], 2-(pyridin-2-yl)imidazo[1,2-a]pyridine[9]possess antitumor activity. Iridium (III) chloride is theimportant platinum group metal ion and has been widely used ashomogeneous catalyst in various redox reactionsdue to its strong catalytic influences. Earlier kinetics and mechanism of Ir(III) catalyzed oxidation of some redox reactions have been reported[10-14].A very few kinetic investigations on the homogeneouslycatalyzed oxidation of ampicillin in alkaline medium are available in literature, therefore, the present mechanistic study for Ir(III)-catalyzed oxidation of ampicillin in alkaline medium by $Cu(Bip)_2^{2+}$ has been undertaken.

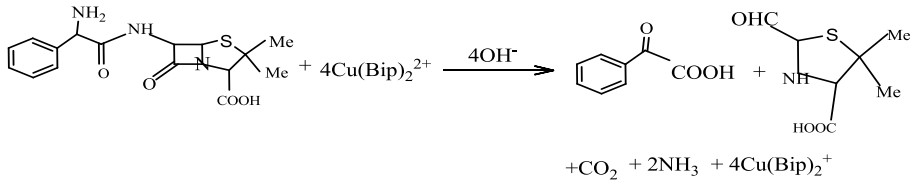
The main objectives of the present study are to ascertain: (i) The influence of the oxidant, substrate and the medium on the reaction kinetics (ii) Catalytic potential of iridium in the oxidation of ampicillin (iii)The possibility of formation of complex or complexes during the course of reaction and (iv)] Oxidative capacity of$Cu(Bip)_2^{2+}$ in the oxidation of ampicillin in the presence of Ir(III) as catalyst

Experimental

Reagent grade chemicals were used. Doubly distilled water was used throughout. A stock solution of $CuSO_4$ was prepared by dissolving a known weight of $CuSO_4$ in double distilled water. The standard solution of ampicillin was freshly prepared. A stock standard solution of Ir(III) chloride was prepared in known acidic strength. Na_2CO_3 and KCl were employed to maintain the required alkalinity and ionic strength, respectively.For kinetic measurements, a Varian Carry Win UV−vis spectrophotometer connected with a Peltier accessory and computer was used. For pH measurement, EUTECH Instrument pH 510 was used.The absorption spectra of the product thatis, $Cu(Bip)_2^{+}$ complex solutions were recorded at the wavelength corresponding to absorption maximum (λmax=410) with molar extinction coefficient 5×10^3 dm^3 mol^{-1} cm^{-1}.One set of reaction mixture containing the reactants$CuSO_4$,Na_2CO_3, Ir(II)-chloride, bipyridyl and KCl and another set having same reactants except $CuSO_4$ were taken in two separate conical flasks, and were placed in a thermostatic water bath at constant temperature of 35 ± 0.1^0C . Solution of amicillin was also kept in another conical flask at the same temperature. When the reaction mixture had attained the required temperature, the calculated amount of ampicillin solution was added in both sets of reaction mixture. Immediately the reaction mixtures were transferred in the quartz cell of 1cm width and placed into the spectrophotometer. The complete reaction mixture acts as absorbing sample and the mixture without $CuSO_4$ solution acts as reference sample. The reaction was studied spectrophotometrically at 35^0C by monitoring the absorbance of $Cu(Bip)_2^{+}$ at 410 nm.

Stoichiometry and product analysis

Various sets of experiments were performed with different$[Cu(Bip)_2^{2+}]$/[Ampicillin] ratios under the condition $Cu(Bip)_2^{2+}$>>[Ampicillin] for 72 h. Determination of unconsumed $Cu(Bip)_2^{2+}$revealed that for the oxidation of each mole of ampicillin, fourmol of $Cu(Bip)_2^{2+}$ were required. Accordingly, the following stoichiometric equation for the oxidation of ampicillin by $Cu(Bip)_2^{2+}$ in presence of alkali is suggested



Results and Discussion

Kinetics of oxidation of ampicillin (Amp) by $Cu(Bip)_2^{2+}$ in alkaline medium by using Ir(III) as homogeneous catalyst have been studied at 35°C. For the determination of order of reaction, the help of Ostwald's Isolation method along with van't Hoff differential method has been taken. The initial rate *i.e.* (−d*c*/d*t*) for each kinetic run was calculated by the slope of the tangent of the plot between remaining $[Cu(II)^*]$ and time drawn at fixed $[Cu(II)^*]$ except that in $[Cu(II)^*]$ variation where tangent was drawn at fixed time. The pseudo first-order rate constant (k_1) was calculated as

$$k_1 = - \frac{dc/dt}{[Cu(II)^*]}$$

where Cu(II)* represents $Cu(Bip)_2^{2+}$.

The reaction under investigation follows first-order kinetics with respect to $[Cu(II)^*]$ as shown by the plot of -dc/dt vs $[Cu(II)^*]$ (Figure 1). First order dependence of the reaction rate at lower [Amp] tends to zero-order at its higher concentrations (Figure 2). The first-order rate constant (k_1) increases with the increase in [Ir(III)], suggesting first order dependence of the reaction on [Ir(III)]. This observation is further confirmed by the straight line passing through the origin in the plot of k_1 vs [Ir(III)] (Figure 3). Straight line passing through

the origin in the plot of k_1 vs $[OH^-]$, indicates first-order dependence of reaction rate on $[OH^-]$ throughout its variation (Figure 4). The order in [bipyridyl] was found to be zero since there is almost no change in the value of k_1 with the change in [bipyridyl] for the aforesaid redox reaction. Variation in ionic strength of the medium has no effect on the rate of reaction. The change in dielectric constant of the medium was ensured by the addition of ethyl alcohol 5 - 20 % to the reaction mixture. On the basis of observed kinetic data it is concluded that pseudo-first-order rate constant increases with the decrease in dielectric constant of the medium. When a plot was made between log k_1 and 1/D values, straight line having an intercept on log k_1 axis with positive slope was obtained (Figure 5). This shows that the reaction is taking place between twooppositely charged ions resulting in the formation of an activated complex. The reaction was studied at four different temperatures i.e., 30, 35, 40 and 45^0C. The rate constants calculated at different temperatures were utilized to calculate various activation parameters. The values of activation parameters like $\Delta G^{\#}$, $\Delta H^{\#}$, $\Delta S^{\#}$ and A for Ir(III)-catalysed oxidation of ampicillin were calculated as 30.61 kJmol^{-1}, 59.07 KJmol^{-1}, 22.00 eu and 9.58 x 10^{17} mol^{-3}dm^{9}sec^{-1} respectively.

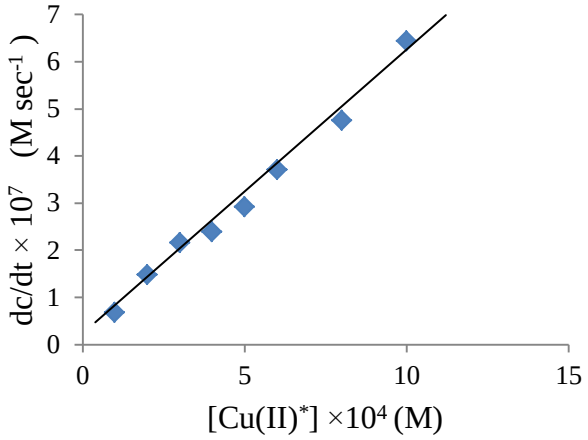


Fig.1.Plot between –dc/dt and [Cu(II)*] at 35^0C.

[Amp] = 2.00 × 10^{-3}M, [Free Bip] = 1.20 × 10^{-3} M, [Ir(III)] = 12.00 ×10^{-7} M, [Na_2CO_3] = 5.00 × 10^{-2} M, μ = 0.85 M

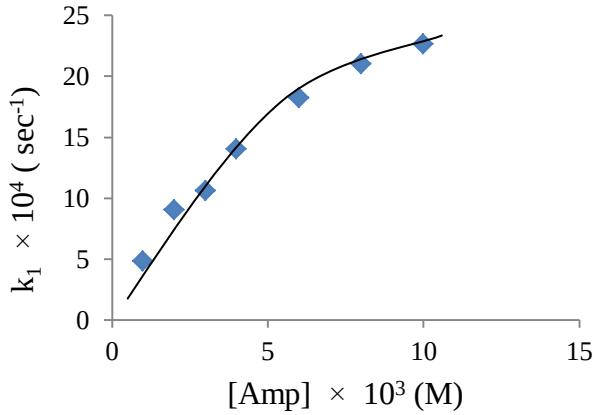


Fig.2.Plot between k_1 and [Amp] at 35^0C.

[Ir(III)] = 12.00 × 10^{-7} M, [Cu(II)*] = 4.00 × 10^{-4} M, [Free Bip] = 1.20 × 10^{-3} M**,** [Na_2CO_3] = 5.00 × 10^{-2} M, μ = 0.85M

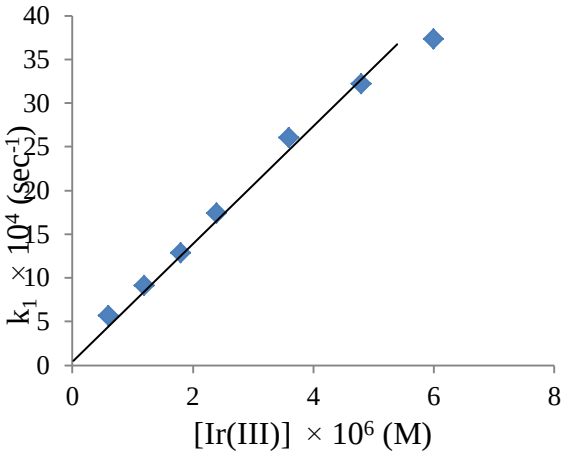


Fig.3.Plot between k_1 and [Ir(III)] at 35^{0}C.

[Amp] = 2.00 × 10^{-3} M, [Cu(II)*] = 4.00 × 10^{-4} M, [Free Bip] = 1.2.00 × 10^{-3} M**,** [Na_2CO_3] = 5.00 × 10^{-2} M, μ = 0.85M

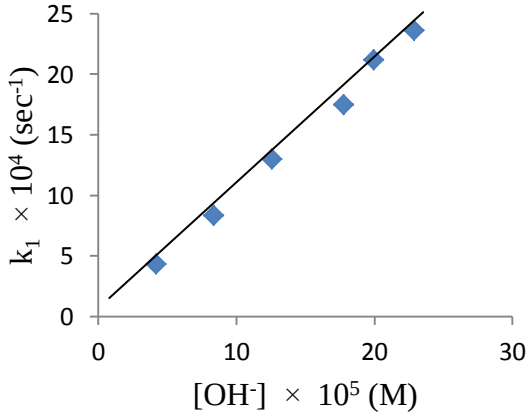


Fig.4.Plot between k_1 and [OH$^-$] at 35^{0}C.

[Ir(III)] = 12.00 × 10^{-7} M, [Amp] = 2.00 × 10^{-3} M, [Cu(II)*] = 4.00 × 10^{-4} M, [Free Bip] = 1.20 × 10^{-3} M**,** μ = 0.85M

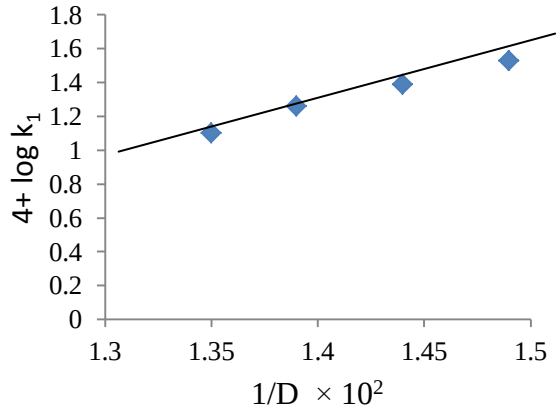


Fig.5.Plot between 4+logk_1 and 1/D at 35^{0}C.

[Ir(III)] = 12.00 × 10^{-7} M, [Amp] = 2.00 × 10^{-3} M, [Cu(II)*] = 4.00 × 10^{-4} M, [Free Bip] = 1.20 × 10^{-3} M**,** [Na_2CO_3] = 5.00 × 10^{-2} M, μ = 0.85M

Reactive species of Cu(II) in alkaline medium

In the present study, Copper(II) has been usedwith bipyridyl as complexing agent in alkaline medium. On the basis of kinetic results obtained and spectrophotometric evidence collected, it is assumed that the reactive species of Cu(II) is $[Cu(Bip)_2]^{2+}$ instead of free Cu(II). Formation of the complex, $[Cu(Bip)_2]^{2+}$, is confirmed by its absorption at λmax 670 nm with molar extinction coefficient 0.59×10^2 dm^3 mol^{-1} cm^{-1}, which is also supported by literature[15].

Reactive species of Ir(III) in alkaline medium

The study concerning the separation of rhodium and iridium and chlorination of Ir(III) and Ir(IV) is reported[16].This study was concerned with the effect of HCl concentration and temperature on iridium(III) speciation at equilibrium. In this study, it is reported that at room temperature and at 70ºC, Ir(III)-chloride in 0.1M HCl concentration remains in the form of $IrCl_3(H_2O)_3$ while at 1.4 M HCl concentration it remains in the form of $IrCl_3(H_2O)_3$ at room temperature and in the form of $[IrCl_4(H_2O)_2]^-$ at 70ºC . This report further says that at 4M HCl concentration iridium (III) will exist mainly in the form of $[IrCl_4(H_2O)_2]^-$ at room temperature.

In the present study, the solution of the catalyst, Ir(III)-chloride, has been prepared in 0.1 M HCl.In view of the above, the starting species may be assumed to be $[IrCl_3(H_2O)_3]$ in the present investigation. Further since the study, for the catalyzed oxidation of ampicillin has been made in alkaline medium hence decision about the reactive species of Ir(III) chloride can be taken only after taking into account the effect of $[OH^-]$ on the rate of oxidation. On the basis of observed first-order kinetics in OH^- and increase in absorbance from 2.658 to 2.81 and 2.87 of Ir(III) chloride solution and Ir(III)-chloride solution with two different concentrations of OH^- (Fig. 6) in the oxidation of ampicillin, it can be concluded that the following equilibrium is in existence in the reaction under investigation.

$$[IrCl_3(H_2O)_3] + OH^- \rightleftharpoons [IrCl_3OH(H_2O)_2]^- + H_2O$$

Out of two species, $[IrCl_3(H_2O)_3]$ and $[IrCl_3OH(H_2O)_2]^-$, the species$[IrCl_3OH(H_2O)_2]^-$ can be assumed as the reactive species of Ir(III)-chloride in the oxidation of ampicillin because only with the reactive species$[IrCl_3OH(H_2O)_2]^-$and with the existence of above equilibriumin the reaction, a rate law showing positive effect of $[OH^-]$ on the rate of oxidation can be derived.

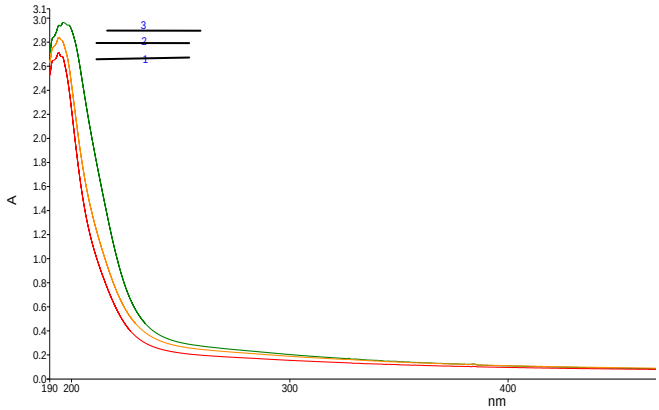
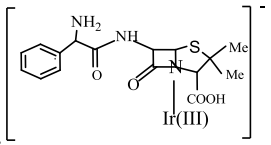
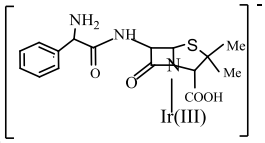
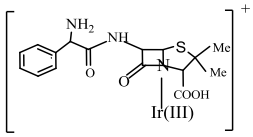


Fig 6. Spectra of solutions recorded at room temperature.

(1) [Ir(III)] = 3.35 x 10^{-5} M (2) [Ir(III)] = 3.35 x 10^{-5} M, $[Na_2CO_3]$ = 1.00 X 10^{-2}M (3) [Ir(III)] = 3.35 x 10^{-5} M, $[Na_2CO_3]$ = 2.00X10^{-2}M

Spectrophotometric evidence for the formation of complex or complexes during the course of reaction

For finding out the possibility of formation of a complex between ampicillin and the reactive form of Ir(III)-chloride, spectra of solutions containing ampicillin and Na_2CO_3 and also ampicillin, Na_2CO_3 and two different concentrations of Ir(III)-chloride were recorded (Fig. 7). From Fig. 7, it is evident that with the increase in Ir(III)-chloride concentration, there is an increase in absorbance from 0.21 to 0.26, indicating formation of a complex between ampicillin and reactive species of Ir(III)-chloride, $[IrCl_3(H_2O)_2OH]^-$. Step (I) of

proposed scheme-1 clearly shows the formation of a compex C_2, i.e.  , between ampicillin and $[IrCl_3(H_2O)_2OH]^-$. Further, when an attempt was made to ascertain the possibility of formation of a complex between C_2, i.e.,  , and $Cu(Bip)_2^{2+}$ in alkaline medium, it is found that there is an increase in absorbance from 0.33 to 0.38, 0.40, 0.43 and 0.46 for the spectra recorded for solutions of ampicillin, Na_2CO_3 and $[IrCl_3(H_2O)_2OH]^-$ as well as for solutions containing ampicillin, Na_2CO_3, $[IrCl_3(H_2O)_2OH]^-$ and five different concentrations of $Cu(Bip)_2^{2+}$. The increase in absorbance with the increase in concentrations of $Cu(Bip)_2^{2+}$ support the formation of C_3, i.e.,  , through Step (II) of the proposed Scheme-1.

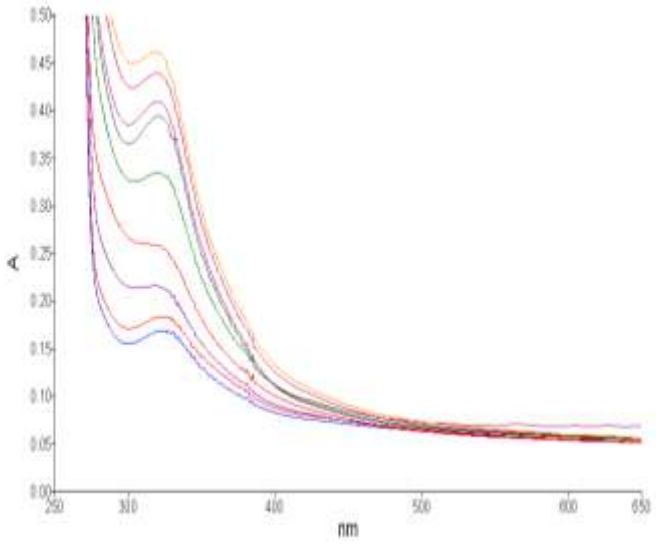
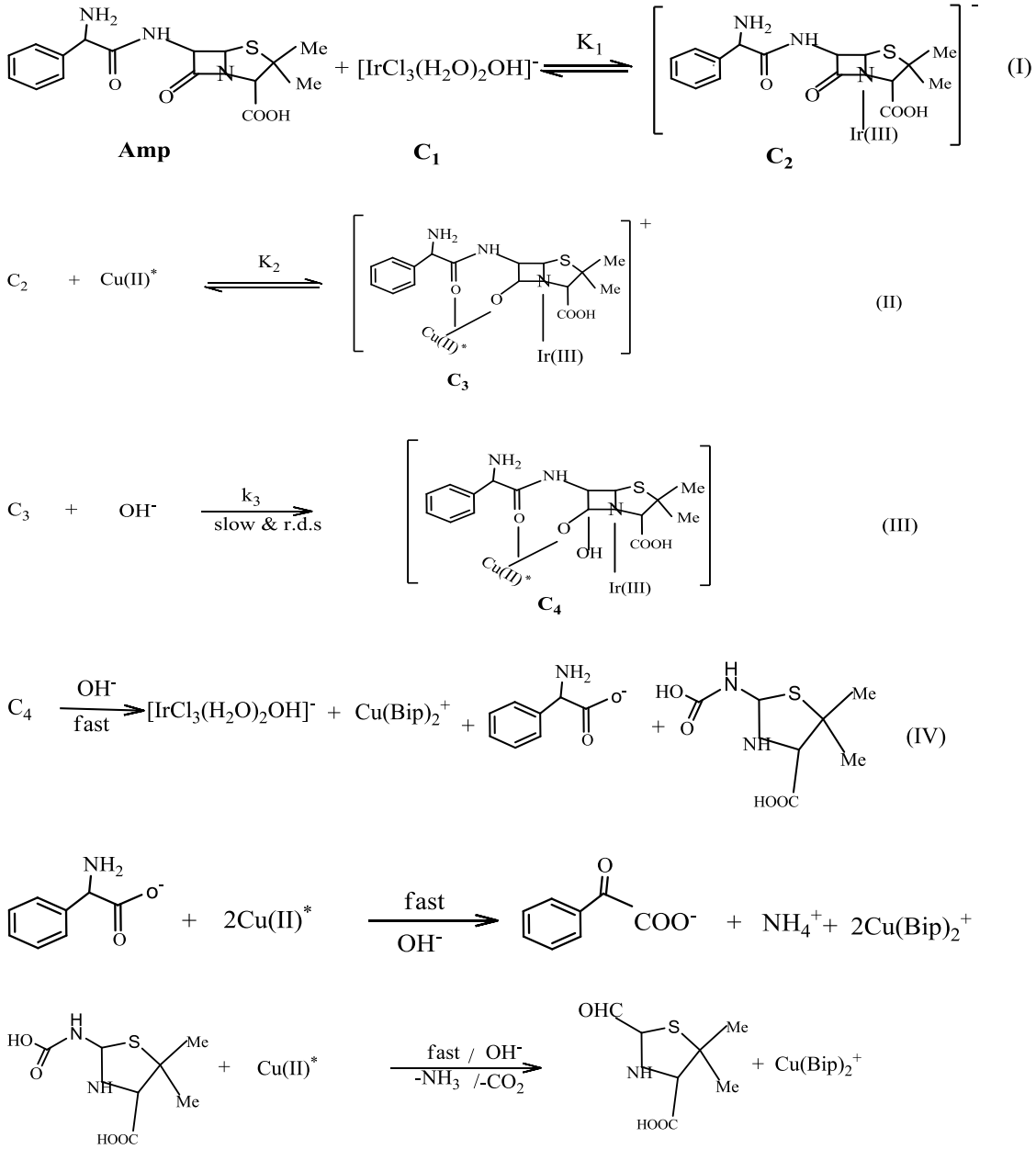


Fig 7. Spectra of solutions recorded at room temperature.(1) [Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 2.00 x10^{-2} M (2) [Amp] = 2.00 x 10^{-2} M,[Na_2CO_3] = 4.00 X 10^{-2} M (3) [Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 4.00 x 10^{-2}, [Ir(III)] = 3.00 x 10^{-5} M, (4) [Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 4.00 X 10^{-2} M, [Ir(III)] = 6.00 x 10^{-5}M (5) [Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 4.00 X 10^{-2},[Ir(III)] = 6.00 x 10^{-5}M[Cu(II)*] = 1.00 x 10^{-4}M, [Free Bip] = 1.20 x 10^{-3} M (6)[Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 4.00 X 10^{-2},[Ir(III)] = 6.00 x 10^{-5}M[Cu(II)*] = 2.00 x 10^{-4}M, [Free Bip] = 1.20 x 10^{-3} M (7) [Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 4.00 X 10^{-2},[Ir(III)] = 6.00 x 10^{-5}M[Cu(II)*] = 3.00 x 10^{-4}M, [Free Bip] = 1.20 x 10^{-3} M (8)[Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 4.00 X 10^{-2},[Ir(III)] = 6.00 x 10^{-5}M[Cu(II)*] = 4.00 x 10^{-4}M, [Free Bip] = 1.20 x 10^{-3} M (9)[Amp] = 2.00 x 10^{-2} M, [Na_2CO_3] = 4.00 X 10^{-2},[Ir(III)] = 6.00 x 10^{-5}M[Cu(II)*] = 5.00x10^{-4}M, [Free Bip]=1.20x10^{-3} M

Taking into consideration the observed kinetic orders with respect to reactantsinvolved, spectrophotometric evidence collected forthe formation of complexes during the course of reaction, effect of dielectric constant of themedium on the rate of oxidation and also the positive entropy of activation,a most probable mechanism in the form of Scheme-1can be proposed for the Ir(III)-catalysed oxidation of ampicillin by$Cu(Bip)_2^{2+}$ in alkaline medium.

Scheme-1



On the basis of the above reaction scheme the rate in terms of decrease in concentration of $Cu(II)^*$ can be expressed as

$$\text{Rate} = \frac{-d[Cu(II)^*]}{dt} = 4k_3[C_3][OH^-] \qquad (1)$$

where 4 indicates that one mole of ampicillin is oxidizedby 4 moles of $Cu(II)^*$.

On applying the law of chemical equilibrium to steps (I) and(II), the equations for the concentrations of C_2 and C_3can be obtained in the following way

$[C_2] = K_1[Amp][C_1]$ (2)

$[C_3] = K_2[C_2][Cu(II)^*]$(3)

According to the reaction scheme-1, the total concentration of Ir(III) *i.e.* $[Ir(III)]_T$ can be expressed as:

$[Ir(III)]_T = [C_1] + [C_2]$(4)

with the help of Eqs. (1), (2), (3) and (4), we obtain Eq. (5)

$$\text{Rate} = \frac{-d[Cu(II)^*]}{dt} = \frac{4k_3K_1K_2[Cu(II)^*][Ir(III)]_T[OH^-][Amp]}{1+K_1[Amp]} \quad (5)$$

Equation (5) is the final rate law which is in complete accordance with our experimental findinds.

Eq. (5) can also be written as eq. (6)

$$\frac{[Ir(III)]_T[Cu(II)^*][OH^-]}{\text{Rate}} = \frac{1}{4k_3K_1K_2[Amp]} + \frac{1}{4k_3K_2} \quad (6)$$

According to eq. (6), when a plot was made between $\frac{[Ir(III)]_T[Cu(II)^*][OH^-]}{\text{Rate}}$ and $\frac{1}{[Amp]}$, a straight line having positive intercept on y-axis has been obtained (Fig 8). This clearly proves the validity of rate law (5) and hence the proposed reaction Scheme-1. From the slope and intercept of straight line the values of K_1 and$k_3K_2$were calculated and found as 1.41 x 10^2 $mol^{-1}dm3$ and 2.9 x 10^7 $mol^2dm^{-6}sec^{-1}$, respectively. Using these values ofK_1 and$k_3K_2$and the rate law (5), the initial rate of the reaction i.e. $-d[Cu(II)^*]/dt$ for each kinetic run has been calculated in the variation of [Amp] and found in close conformity with the observed rate of reaction (Table-1). This further confirms the validity of the rate law (5) and hence the proposed reaction Scheme-1.

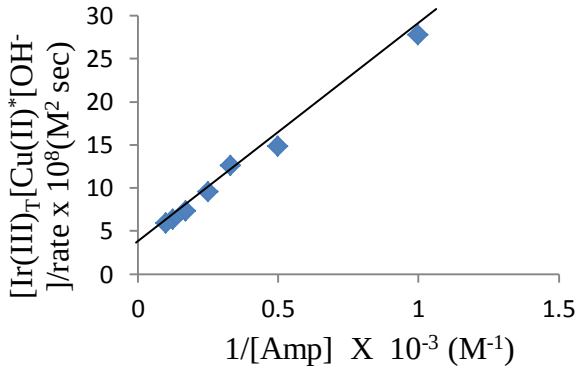


Fig. 8. Plot between $\frac{[Ir(III)]_T[Cu(II)^*][OH^-]}{\text{Rate}}$ and $\frac{1}{[Amp]}$ at 35^0C.

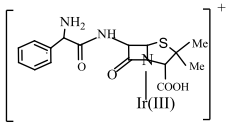
$[Ir(III)] = 12.00 \times 10^{-7}$ M, $[Amp] = 2.00 \times 10^{-3}$ M, $[Cu(II)^*] = 4.00 \times 10^{-4}$ M, [Free Bip] = 1.20×10^{-3} M**,** $[Na_2CO_3] = 5.00 \times 10^{-2}$ M, $\mu = 0.85$M

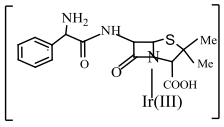
Table-1: Experimental and Calculated values of the rate for the variations of [Amp] $[OH^-]$ and [Ir(III)] in the Ir(III)-catalyzed oxidation of ampicillin by $Cu(Bip)_2^{2+}$ at 35^0C

[Amp] $\times 10^3$(M)	**[Ir(III)]$\times 10^6$(M)**	**$[OH^-] \times 10^5$ (M)**	**-dc/dt$\times 10^7$(Msec^{-1})**		
			Experimental rate	**Rate calculated on the basis of rate law(equation(5))**	**Rate calculated on the basis of multiple regression analysis**
1.00	1.20	8.38	1.45	1.46	1.68
2.00	1.20	8.38	2.71	2.60	2.67
3.00	1.20	8.38	3.19	3.52	3.44
4.00	1.20	8.38	4.21	4.26	4.14

6.00	1.20	8.38	5.47	5.42	5.33
8.00	1.20	8.38	6.31	6.27	6.41
10.00	1.20	8.38	6.80	6.92	7.36
2.00	0.60	8.38	1.70	1.30	1.40
2.00	1.20	8.38	2.75	2.61	2.67
2.00	1.80	8.38	3.86	3.91	3.78
2.00	2.40	8.38	5.23	5.21	4.98
2.00	3.60	8.38	7.81	7.82	7.03
2.00	4.80	8.38	9.67	10.43	9.27
2.00	6.0	8.38	10.61	13.04	11.14
2.00	1.20	4.20	1.29	1.31	1.34
2.00	1.20	8.38	2.50	2.61	2.67
2.00	1.20	12.6	3.90	3.92	3.95
2.00	1.20	17.78	5.24	5.53	5.59
2.00	1.20	19.95	6.36	6.21	6.27
2.00	1.20	22.90	7.08	7.12	7.03

Solutions conditions; $[Cu(II)^{*}] = 4.00 \times 10^{-4}$, [Free Bip] = 1.20×10^{-3} M, $\mu = 0.85$M

It is reported[17]thatwhen reaction occurs between two oppositely charged species, the transition state becomes less polar than the initial state. In the present investigation, observed positive entropy of activation in the oxidation of ampicillin clearly supports the interaction between charged species, C_3, i.e. 

, andOH^- in the rate determining step leading to the formation of a less polar activated complex, C_4, i.e. 

, which ultimately converts into products via several fast steps. This is also supported by the spectroscopic evidence collected for the formation of complex, C_4, in the step (III) of the proposed reaction Scheme 1.

Multiple regression analysis

Experimental kinetic data for the variation of [Amp], $[OH]^-$ and [Ir(III)] were analyzed for Multiple Regression Analysis. On the basis of equation (7) of fitted model obtained by multiple regression analysis for ampicillin, the rates for the variation of [Amp], $[OH^-]$ and [Ir(III)] were calculated and found in close agreement with the experimental rates and the rates calculated on the basis of rate law (5) Table 1. This gives support to the proposed rate law (5) and hence the proposed mechanism. The equation of the fitted model is

Col_1 = 7.98374 + 0.633799*Col_2 + 0.982237*Col_3 + 0.899112*Col_4 (7)

Where Col_1 = ln k_1, Col_2 = ln [Amp], Col_3 = ln $[OH]^-$ and Col_4 = ln[Ir(III)]

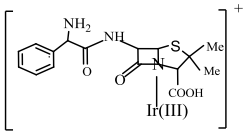
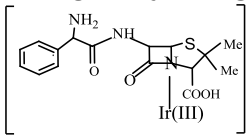
Comparative Studies

The findings of the present study of oxidation of ampicillin by $Cu(Bip)_2^{2+}$ in presence of Ir(III) as homogeneous catalyst have been compared with the results reported for Pd(II) catalyzed[1] oxidation of tetracycline and Ru(III) catalyzed[18] oxidation of lactose by $Cu(Bip)_2^{2+}$ in alkaline medium. When the present study has been made for the effect of $[Cu(II)^{*}]$ on the rate of oxidation, it is found that the rate is directly proportional to $[Cu(II)^{*}]$. Contrary to this, the first to zero order kinetics in $[Cu(II)^{*}]$ was observed for Pd(II)-catalyzed[1] oxidation and no effect of $[Cu(II)^{*}]$ on the rate of reaction was found for Ru(III) catalyzed[18] oxidation. Observed first to zero-order kinetics in [Amp] is contrary to the reported first-order kinetics in

[tetracycline] and [lactose] for Pd(II) catalyzed[1] oxidation of [tetracycline] and Ru(III) catalyzed[18] oxidation of [lactose], respectively. In the present study first-order kinetics with respect to [Ir(III)] has been observed throughout its variation. This result is not similar to the reported fractional positive order kinetics with respect to [Pd(II)]. It is also contrary to the role of Ru(III) as an inhibitor in the oxidation of lactose by $Cu(Bip)_2^{2+}$ in alkaline medium. On the basis of observed kinetic data and spectroscopic evidence, it has been assumed that the species $[IrCl_3(H_2O)_2OH]^-$ is the reactive species of Ir(III)-chloride in the oxidation of ampicillin, whereas $[Pd(OH)Cl_3]^{2-}$ is found as reactive species of Pd(II)-chloride in the oxidation of tetracycline and $[RuCl_2(H_2O)_2(OH)_2]^-$ as the reactive species of Ru(III)-chloride in the oxidation of lactose by $Cu(Bip)_2^{2+}$ in alkaline medium. First order kinetics in $[OH^-]$ in the present study differs from the zero-order kinetics of $[OH^-]$in the Pd(II)-catalyzed[1] oxidation and second-order kinetics tending towards first-order kinetics in the oxidation of lactose[18] using Ru(III) as an inhibitor. The increase in first-order rate constant k_1 with the decrease in dielectric constant of the medium was observed in the present study as well as in the reported[18] oxidation of lactose by $Cu(Bip)_2^{2+}$ in alkaline medium using Ru(III) as an inhibitor. This result is contrary to Pd(II) catalyzed[1] oxidation of tetracycline where it is concluded that there is no effect of dielectric constant of the medium on the rate of reaction. In view of the facts mentioned above, it can be said that the present study is different in many respect from the other two studies reported earlier.

Conclusion

The following conclusions can be derived from the observed kinetic data and spectral information collected for the Ir(III)-catalyzed oxidation of ampicillin by $Cu(Bip)_2^{2+}$ in alkaline medium:

1. $Cu(Bip)_2^{2+}$, ampicillin as such and $[IrCl_3(H_2O)_2OH]^-$ have been assumed as the reactive species of Cu(II), ampicillin and Ir(III)-chloride in alkaline medium, respectively.
2. The reaction shows first-order kinetics with respect to[Cu(II)], $[OH]^-$ and [Ir(III)] and fractional positive order kinetics in [Amp].
3. In step (III) of Reaction Scheme-1, an interaction between a charged species,C_3, i.e.  , andnegatively charged OH^- resulting in the formation of most reactive activated complex C_4, i.e.  , is well supported by the observed positive entropy of activation and the effect of dielectric constant of the medium on the rate of oxidation.

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